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PRELIMINARY TESTS WITH CERTAIN N-SUBSTITUTED 2,4-DINITROANILINES AND o-CHLOROBENZAMIDES FOR SYNERGISTIC ACTION IN ALLETHRIN FLY SPRAYS

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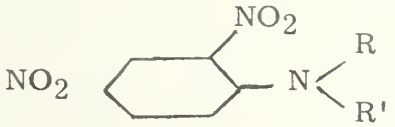
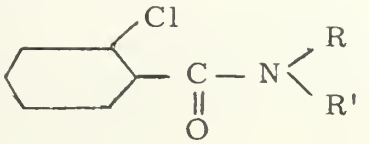
In the search for synergists for pyrethrum and allethrin in fly sprays, the authors have examined a number of compounds in different chemical groups.[1/] A study of the joint action of derivatives of 2,4-dinitroaniline and o-chlorobenzamide with allethrin is described herein.

The 2,4-dinitroanilines were prepared by reacting 1-chloro-2,4-dinitrobenzene with various amines under suitable conditions. They may all be represented by the general formula



The o-chlorobenzamides were prepared by reacting o-chlorobenzoyl chloride with various amines under suitable conditions. They are represented by the general formula



R is a hydrogen or alkyl group, and R' is an alkyl, aryl, or cycloaliphatic group in the dinitroaniline derivatives and an alkyl, aryl, or cyclic group in the chlorobenzamide derivatives, with or without substituents.

1/ Previous publications in this series are E-805, E-828, E-837, and E-848.

The compounds were incorporated in sprays, alone and in mixtures with 0.5 mg. of allethrin per milliliter. The concentration of the adjuncts was 5 mg. per milliliter except in those instances where solubility was so low that this concentration could not be obtained. For such materials the concentration was 2.5 mg. per milliliter. Acetone was used as an auxiliary solvent in the proportion of 1 part of acetone to 3 parts of refined kerosene.

Allethrin was employed as the standard of comparison at concentrations of 0.5, 1.0, and 2.0 mg. per milliliter. Its purity was high (94 percent by the hydrogenolysis method).

The tests were made by the Campbell turntable method on laboratory-reared adult house flies (Musca domestica L.). The flies were approximately 3 days old and averaged 100 in each test. The mixed sprays were replicated four times, the sprays containing the adjuncts alone but twice. Since there were too many sprays to be tested at one time, they were tested in a number of series, each with a different population of flies. Because mortalities would not be directly comparable, the allethrin standard sprays were included in each series.

The mortalities for the mixed sprays are given in tables 1 and 2. Knockdown of flies was not estimated, since acetone itself causes high knockdown. The adjuncts alone were not toxic at the concentrations used.

To determine whether synergism existed in the mixed sprays, the following procedure was used: The mortalities obtained for the standard sprays in each series were plotted on log-probability paper and straight lines drawn. From these lines the allethrin equivalents of the mixed sprays were estimated. Estimates of the increase in the mean equivalents (tables 1 and 2) required to show a significant increase in toxicity were obtained from an analysis of variance of the logarithms of the individual equivalents. Since all these equivalents are compared with the concentration of 0.5 mg. of allethrin per milliliter, they give, when multiplied by 2, expressions of relative toxicity. In those series where it was readily apparent from examination of the mortality data that there was no increase in toxicity, no analysis of variance was made.

Since the adjuncts alone caused no mortality at the concentrations used, all increase in allethrin equivalent over the standard was ascribed to synergism. This increase was significant for 12 of the mixtures. Of the 2,4-dinitroanilines the following were effective:

N-allyl-2,4-dinitroaniline
N-amyl-2,4-dinitroaniline
N-sec-butyl-2,4-dinitroaniline

Of the o-chlorobenzamides the following were effective:

N-amyl-o-chlorobenzamide
N-sec-amyl-o-chlorobenzamide
N-butyl-o-chlorobenzamide
2-chloro-m-benzotoluide
o-chloro-N,N-diethylbenzamide
2-chloro-2'-nitrobenzanilide
2-chlorobenzanilide
2,2'-dichlorobenzanilide
2,3'-dichlorobenzanilide

2-Chloro-p-benzotoluide was on the borderline of effectiveness.

The intensity of synergism was not very great for any of the materials. The greatest effect was to raise toxicity to about twice that expected for allethrin alone. This effect was obtained with the following synergists:

N-amyl-2,4-dinitroaniline
N-amyl-o-chlorobenzamide
N-sec-amyl-o-chlorobenzamide

Table 1.--Toxicity to house flies of spice sprays containing certain 2,4-dinitroaniline compounds in mixtures with 0.5 mg. of allethrin per milliliter. Concentration is 5 mg. per milliliter unless otherwise indicated.

Adjunct	Mean mortality in 1 day	Mean allethrin equivalent
	Percent	Mg. per ml.
Series 1		
Aniline, N-N-diethyl-2,4-dinitro-	61.4	-
N-N-diisobutyl-2,4-dinitro-	42.8	-
N-isobutyl-2,4-dinitro-	53.1	-
2,4-dinitro-N-propyl-	59.7	-
Diphenylamine, 3'-chloro-2,4-dinitro-[1/]	54.4	-
Allethrin standard, 0.5 mg. per ml.	58.2	-
1.0	75.6	-
2.0	94.5	-
Series 2		
Diphenylamine, 4'-chloro-2,4-dinitro-	56.2	-
N-ethyl-2,4-dinitro-	45.8	-
N-methyl-2,4-dinitro-	56.8	-
2'-methyl-2,4-dinitro-	56.6	-
3'-methyl-2,4-dinitro-	49.4	-
Allethrin standard, 0.5 mg. per ml.	56.8	-
1.0	79.0	-
2.0	97.3	-
Series 3		
Amine, N-amyl-2,4-dinitro-	67.9	0.873
N-butyl-2,4-dinitro-	41.1	.515
N-ethyl-2,4-dinitro-	42.6	.531
N-methyl-2,4-dinitro-	44.4	.550
Diphenylamine, 4'-methyl-2,4-dinitro-	41.6	.526
Allethrin standard, 0.5 mg. per ml.	44.9	.555
1.0	68.9	.891
2.0	94.9	2.163
Required to show synergism -------		.565

Table 1.--Continued

Adjunct	Mean mortality in 1 day	Mean allethrin equivalent
	Percent	Mg. per ml.
Series 4		
Diphenylamine, 2'-methoxy-2,4-dinitro-[1/]	46.7	0.439
2,4,4'-trinitro-[1/]	63.1	.602
1-Naphthylamine, N-(2,4-dinitrophenyl)-[1/]	42.6	.431
2-Naphthylamine, N-(2,4-dinitrophenyl)-[1/]	57.6	.502
Piperidine, 1-(2,4-dinitrophenyl)-	61.1	.600
Allethrin standard, 0.5 mg. per ml.	52.5	.516
1.0	82.3	.929
2.0	98.7	2.275
Required to show synergism	---------	.624
Series 5		
Aniline, N-isopropyl-2,4-dinitro-	48.9	-
Benzylamine, N-(2,4-dinitroanilino)-	49.6	-
Cyclohexylamine, N-(2,4-dinitrophenyl)-[1/]	48.9	-
Ethanol, 2-(2,4-dinitroanilino)-	46.1	-
Phenol, o-(2,4-dinitroanilino)-	43.4	-
Allethrin standard, 0.5 mg. per ml.	52.2	-
1.0	76.1	-
2.0	98.4	-
Series 6		
Aniline, N-allyl-2,4-dinitro-	55.4	.622
N-sec-butyl-2,4-dinitro-	61.7	.686
Dibenzylamine, N-(2,4-dinitrophenyl)-	32.4	.427
Glycine, N-(2,4-dinitrophenyl)-	37.7	.460
Phenol, p-(2,4-dinitroanilino)-	35.0	.440
Allethrin standard, 0.5 mg. per ml.	41.5	.491
1.0	81.1	.980
2.0	97.6	1.714
Required to show synergism	---------	.602

[1/] 2.5 mg. per milliliter.

Table 2. - Toxicity to house flies of space sprays containing certain o-chlorobenzamides in mixtures with 0.5 mg. of allethrin per milliliter. Concentration is 5 mg. per milliliter unless otherwise noted.

Adjunct	Mean mortality in 1 day	Mean allethrin equivalent
	Percent	Mg. per ml.
Series 1		
Benzamide, o-chloro-	62.4	-
o-chloro-N-ethyl-	59.9	-
o-chloro-N-isopropyl-	64.3	-
o-chloro-N-methyl-	61.5	-
o-chloro-N-propyl-	63.2	-
Allethrin standard, 0.5 mg. per ml.	62.9	-
1.0	89.5	-
2.0	99.0	-
Series 2		
Benzamide, N-benzyl-o-chloro-	66.1	0.593
N-butyl-o-chloro-	78.3	.760
o-chloro-N-isobutyl-	75.1	.718
Morpholine, 4-(o-chlorobenzoyl)-	66.7	.605
Piperidine, 1-(o-chlorobenzoyl)-	74.0	.695
Allethrin standard, 0.5 mg. per ml.	55.5	.497
1.0	88.5	1.021
2.0	98.8	2.500
Required to show synergism		.739
Series 3		
Benzamide, N-amyl-o-chloro-	79.9	1.038
N-sec-amyl-o-chloro-	73.6	.897
N-tert-butyl-o-chloro-	67.9	.753
o-chloro-N-cyclohexyl-	54.7	.551
o-chloro-N,N-dimethyl-	56.2	.573
Allethrin standard, 0.5 mg. per ml.	52.3	.484
1.0	77.7	.968
2.0	95.0	2.218
Required to show synergism		.779

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Table 2.--Continued

Adjunct	Mean mortality in 1 day	Mean allethrin equivalent
	Percent	Mg. per ml.
Series 4		
Benzamide, o-chloro-N,N-diethyl-	64.0	0.741
Benzanilide, 2-chloro-	58.4	.711
2,2'-dichloro-	67.0	.780
2,3'-dichloro-	45.3	.746
Phenylhydrazine, 1-(o-chlorobenzoyl)-[1/]	54.0	.557
Allethrin standard, 0.5 mg. per ml.	43.4	.522
1.0	76.7	.980
2.0	96.8	2.163
Required to show synergisn	---	.672
Series 5		
Benzanilide, 4'-bromo-2-chloro-	56.2	.542
2-chloro-2'-nitro-	64.0	.750
2,4'-dichloro-	56.9	.548
2,2,'5'-trichloro-	58.1	.560
p-Benzanisidide, 2-chloro-	46.2	.465
Allethrin standard, 0.5 mg. per ml.	55.9	.537
1.0	78.8	.923
2.0	96.8	2.173
Required to show synergism	---	.657
Series 6		
Benzanilide, 2-chloro-3'-nitro-	37.7	.428
2-chloro-4'-nitro-	47.5	.531
o-Benzotoluide, 2-chloro-	40.9	.465
m-Benzotoluide, 2-chloro-	56.2	.679
p-Benzotoluide, 2-chloro-	54.7	.622
Allethrin standard, 0.5 mg. per ml.	44.3	.493
1.0	74.6	.984
2.0	93.8	2.208
Required to show synergism	---	.624

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Table 2.--Continued

Adjunct	Mean mortality in 1 day	Mean allethrin equivalent
	Percent	Mg. per ml.
Series 7		
Benzamide, N,N-dibenzyl-o-chloro-	42.5	-
o-Benzanisidide, 2-chloro-	45.2	-
Allethrin standard, 0.5 mg. per ml.	38.1	-
1.0	78.9	-
2.0	95.8	-

1/ 2.5 mg. per milliliter.